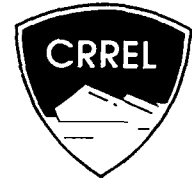


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Surface Changes in Well Casing Pipe Exposed to High Concentrations of Organics in Aqueous Solution

Susan Taylor and Louise Parker

March 1990

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Special Report 90-7



**U.S. Army Corps
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Cold Regions Research &
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PREFACE

This report was prepared by Susan Taylor, Research Scientist, Geological Sciences Branch, Research Division, and Louise Parker, Research Scientist, Applied Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory. This project was funded by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland (R-90 Multi-Analytical Services), Martin H. Stutz, Project Manager.

The authors thank Bob Forest and Dennis Lambert for cutting the casing materials. Thanks also go to Marianne Walsh who made many helpful comments on the draft manuscript and Dr. Thomas Jenkins and Alan Hewitt for reviewing the final draft.

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CONTENTS

Preface	iii
Introduction	1
Materials and methods	1
Results and discussion	3
Visual observations	3
SEM observations	3
Conclusions	4
Literature cited	4
Abstract	15

ILLUSTRATIONS

Figure

1. Low magnification photographs of the four casing surfaces (8×)	5
2. SEM micrograph of untreated PVC (2000×)	6
3. Micrographs of PVC soaked in the test solution (2000×)	6
4. Micrographs of PVC soaked in well water (2000×)	7
5. Micrograph of untreated PTFE (200×)	7
6. Micrographs of PTFE soaked in the test solution (200×)	8
7. Micrographs of PTFE soaked in well water (200×)	9
8. Micrograph of untreated SS316 (200×)	10
9. Micrographs of SS316 soaked in the test solution (200×)	10
10. Micrographs of SS316 soaked in well water (200×)	11
11. Micrograph of untreated SS304 (200×)	11
12. Micrographs of SS304 soaked in the test solution (200×)	12
13. Micrographs of SS304 soaked in well water (200×)	13
14. Micrographs of SS304 (2000×)	14

Surface Changes in Well Casing Pipe Exposed to High Concentrations of Organics in Aqueous Solution

SUSAN TAYLOR AND LOUISE PARKER

INTRODUCTION

Prior to 1985 polyvinyl chloride (PVC) was the most commonly used well casing material for ground water monitoring. In 1985 the EPA published the initial draft of the *Resource Conservation and Recovery Act (RCRA) Ground-Water Monitoring Technical Enforcement Guidance Document*. This document stated that "steel casings deteriorated in corrosive environments; PVC deteriorated in contact with ketones, esters and aromatic hydrocarbons..." and recommended that either Teflon or stainless steel 316 be used for constructing wells. The EPA's concerns were that PVC and the casing materials commonly used for ground water monitoring either altered the ground water samples or did not meet the long-term structural characteristics required of RCRA monitoring wells.

While we have found many studies that have examined the effects of well casing materials on ground water samples (Miller 1982, Curran and Tomson 1983, Houghton and Berger 1984, Reynolds and Gillham 1985, Barcelona and Helfrich 1986, Parker and Jenkins 1986, Sykes et al. 1986, Jones and Miller 1988, Hewitt 1989, Parker and Jenkins, in press), little information exists on the long-term stability of casing materials exposed to extreme environmental conditions such as high salinity or pH, or to either pure or high concentrations of organic solvents.

Schmidt (1987) studied the long-term stability of PVC in contact with gasoline. Sections of rigid, 2-inch-diameter, Type I PVC screen (0.006 slot size) were placed directly in several different grades of gasoline and allowed to sit for 6 months. After these pieces of screen were removed from the gasoline, they were photographed using a scanning electron microscope (SEM) to document any changes in the size of the slot opening or any other changes. Schmidt did not find any changes and concluded that Schedule 40, rigid, Type I PVC can be used when monitoring for the occurrence of gasoline in the water table, a conclusion that agreed with his field experience.

The Nalge Company lists the chemical resistance, compiled from in-house tests, of a number of plastics including PVC and fluorinated resins.* PVC is not

recommended for approximately half of the predominantly organic substances listed, whereas fluorinated resins (FEP, TFE and PFA) are listed as unaffected by 99% of the compounds. Some of the tests were conducted using thin-walled bottles, and the results may not apply to the rigid pipe used for ground water monitoring. It is therefore difficult to use this table without knowledge of how the tests were conducted, and this is proprietary information.

Our study was undertaken to assess how the surface structural characteristics of four common well casing materials—PVC, Teflon (polytetrafluoroethylene, PTFE), stainless steel 304 (SS304) and stainless steel 316 (SS316)—are affected by exposure to high concentrations of organic chemicals in ground water. To check for surface structural changes, pieces of casing were examined with an SEM after being immersed for 1 week, 1 month and 6 months in an aqueous solution containing tetrachloroethylene, toluene, *p*-dichlorobenzene and *o*-dichlorobenzene. These substances are EPA priority pollutants because they often occur in ground water.

MATERIALS AND METHODS

The PVC and stainless steel pipe were obtained from Johnson Well Screen and the PTFE pipe from MIP Inc. The casings are manufactured to meet certain specifications (PVC: ASTM F480-81; SS304 and SS316: ASTM A312[†]; Teflon is not made to an ASTM specification, but the manufacturers check its density, tensile strength and elongation^{**}). Only casings manufactured specifically for ground water monitoring were tested in this study. Small sections, approximately 1.0 cm by 1.0 cm, were cut from each type of casing. The exact dimensions varied with the thickness of the well casing so that the surface areas for the four casing materials would be the same. The dimensions of the sample pieces were limited by the size of the SEM's sample port.

To remove any contamination derived from the

* Personal communication with the Nalge Company.

† Personal communication with Johnson Well Screen.

** Personal communication with MIP Inc.

cutting, all the samples were placed in a solution of deionized water and detergent and sonicated for 10 minutes. They were then rinsed with deionized water until there were no suds and sonicated again in fresh deionized water for 20 minutes. After being rinsed with fresh deionized water, the samples were drained and allowed to air dry on paper towels. This cleaning procedure worked well; no dirt or soap was seen on the samples when examined with the SEM.

The aqueous test solution was prepared by dissolving *p*-dichlorobenzene, *o*-dichlorobenzene, toluene and tetrachloroethylene in a sample of ground water obtained from a local deep well. The concentrations were 17.3, 33.5, 138 and 35.0 mg/L, respectively, approximately one fourth the solubility of each compound in water. The high concentrations of the organics in a single aqueous solution provide a "worst case" scenario, short of chemical attack by a pool of undiluted organic solvent, a situation rarely encountered in ground water monitoring.

Aside from being EPA priority pollutants, the organics were selected because, according to the Nalge Table, all these solvents degrade PVC in their pure form. Tetrachloroethylene was selected because of its apparent preferential rate of sorption (Miller 1982). Its highly planar structure might allow tetrachloroethylene to more easily penetrate the pores of a polymer (Parker and Jenkins 1986). The two isomers of dichlorobenzene and toluene were selected to cover a range in polarity and molecular structure.

For each casing material, six pieces were placed into each of two 40-mL vials and filled with the aqueous test solution. No head space was left, and the vials were capped with a Teflon-lined plastic cap. Control samples were identical except that they were filled with the well water. The samples were stored at room temperature in the dark. Although no biocide was added to prevent biodegradation of the test solution, bacteria were not observed on any of the samples examined by SEM, and the solutions remained clear.

A Hitachi S500 scanning electron microscope was used to examine the samples. The SEM was chosen over other microscopic techniques because of its wide range of magnifications and its good depth of field. A thin layer of gold and palladium was evaporated onto the PVC and PTFE casing surface to make the samples conductive. This thin film is needed to prevent thermal and radiation damage of the sample's surface and does not significantly change the surface structure of the sample (Goldstein et al. 1981). The two stainless steel samples, being good conductors, did not need to be coated. An acceleration voltage of 20 keV was used.

In addition to images of the sample's surface, a Kevex energy dispersive spectrometer allowed quali-

tative elemental analyses to be made of points or areas of the surface. However, only those elements heavier than sodium can be detected, so the plastics could not be analyzed using this technique.

For each of the four well casing materials, samples that had been exposed to the test solution for 1 week, 1 month and 6 months were examined with the SEM and compared with the control samples. Pieces of casing that had not been placed in any aqueous solution were also examined and are assumed to be representative of the initial structure of the casing's surface. Only the inside wall of the casing was examined.

SS316 and PTFE were photographed at 35 \times and 200 \times magnification, and PVC and SS304 at 200 \times and 2000 \times magnification. These magnifications highlighted the surface structure of each sample, and since all samples were photographed at 200 \times magnification, it allowed all the samples to be compared.

Originally only two of the six samples of each type of well casing were examined with the SEM. However, because a number of changes were observed in the PVC and SS304 samples and we could not tell whether the changes were caused by the organic solution or by intersample variation, all six of the test, control and untreated SS304 and PVC samples were examined. As it was still unclear whether changes seen on the SS304 surface were due to the organics, two untreated SS304 samples were photographed and then placed in a test solution to be reexamined and rephotographed after 6 months in the test solution. This method was not used initially because the plastics need to be coated prior to SEM examination and could not have been treated the same way as the stainless steel samples.

RESULTS AND DISCUSSION

Visual observations

Visual inspection of PVC casings showed them to be quite smooth except for fine grooves running parallel to the casing's length. These linear features are the result of the extrusion method used to manufacture the well casing. The PTFE samples, like the PVC, have little surface relief, but unlike the PVC, the PTFE samples have a patterned surface (rough areas alternating with smooth areas). Both stainless steel samples are characterized by a matt surface texture, but SS316 has more surface relief than the SS304 (Fig. 1).

Since some of the stainless steel samples had rust spots (1 of 12 SS316 samples and 2 of 12 SS304 samples had one or more spots), only samples that appeared to be free of defects, rusting, gouges or scratches were selected to be studied with the SEM. However, despite this preliminary screening, a dark, smooth, patchy coat-

ing was observed on some of the SS304 samples studied with the SEM. Energy dispersive X-ray analysis showed the coating to be aluminum. This coating probably came from the aluminum plug placed inside the well casing when the samples were cut on the lathe. Casing pieces having aluminum coatings were replaced by other samples for study.

SEM observations

PVC

Examination of the untreated PVC casings with the SEM shows them to have smooth, slightly lined surfaces marred by an even distribution of irregularly shaped holes (Fig. 2). These holes are approximately 5 μm along their longest dimension. The surface between the holes had dimples that appeared to have the same geometry as the larger holes. No change in surface structure was observed between the 1 week, 1 month, 6 month test samples (Fig. 3), the untreated samples (Fig. 2) and the control samples (Fig. 4). The bright particles in the holes and on the surface in Figure 4 are particulates that were present in the well water.

PTFE

Untreated PTFE casings have smooth areas interrupted by patches of pulled-out fibrous strands paralleling the length of the tube (Fig. 5). The surface characteristics of the PTFE varied from sample to sample, with large changes in both the size and the number of fibrous patches. Test samples (Fig. 6) could not be distinguished from control samples (Fig. 7); however, the lack of regular features makes it difficult to identify any alterations which might have been caused by immersion in the test solution.

SS316

SS316 casings have a rough surface, with finger-like protrusions sticking out from the surface (Fig. 8). The surface area of these samples should be greater than that of the SS304, and Hewitt (1989) found that it rusted more rapidly than SS304. Magnifications higher than 200 \times showed no detail in the areas between the protrusions, so lower magnifications were used to characterize the surface. At a magnifications of 35 \times and 200 \times , no changes were seen between the 1 week, 1 month and 6 month test samples (Fig. 9) and the control samples (Fig. 10).

SS304

SS304 showed some change among the untreated, test and control samples. Specific surface changes appeared to be related to long-term residence in the test solution, since the untreated (unwetted) samples generally had a patterned surface composed of discrete cells

or units separated by troughs (Fig. 11) and this structure is less distinct on samples exposed to the test solution (Fig. 12) as compared to those exposed to well water (Fig. 13). However, micrographs taken at random places on each of the six duplicate samples of the untreated, 6-month test and 6-month control samples show that the patterned surface is not unique to untreated or control samples and occurs on two of the six test samples. Similarly the less-structured features can be seen on one of the untreated samples and on one of the control samples.

To resolve what effect the test solution has on SS304, we began an additional experiment. In this test, two samples were examined and photographed prior to exposure. The same areas were reexamined after 6 months of contact with the test solution using a magnification of 35 \times , 200 \times and 2000 \times . Neither sample showed any change (Fig. 14).

The observations presented above indicate that the surface characteristics of PVC, PTFE, SS316 and SS304 do not change when exposed to a concentrated organic aqueous solution. Because of the lack of distinguishing features at high magnification, PTFE and SS316 were examined at a lower magnification; consequently, small changes that might have occurred may not have been seen. It was particularly difficult to assess whether or not changes had occurred on PTFE. However, no obvious changes (swelling, pitting etc.) were seen.

Our work is preliminary, as the variability, both casing to casing and manufacturer to manufacturer, was not addressed. This potential variability needs to be taken into account when using our results for predictive purposes.

CONCLUSIONS

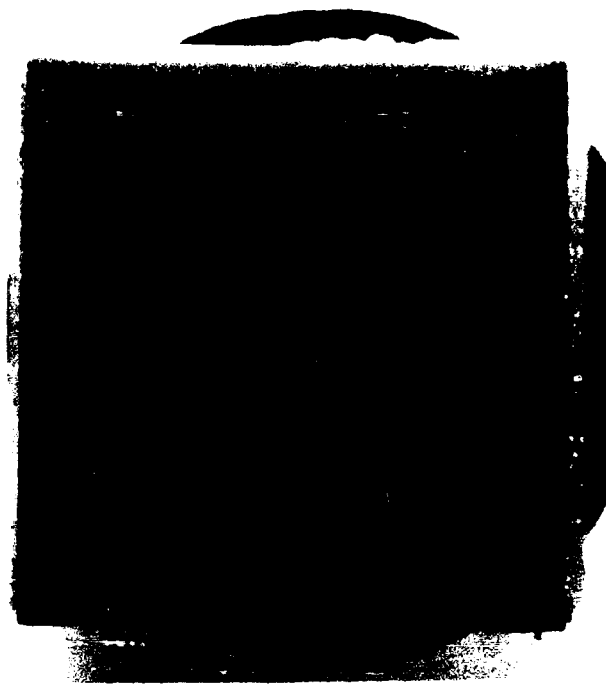
Small sections of well casing were examined with an SEM to determine how they were affected by exposure to an aqueous solution containing high concentrations of organics thought to degrade PVC and chlorinated compounds known to be sorbed by both PVC and Teflon casings. The surface structure of the PVC, SS304 and SS316 was apparently unaffected by the test solution. PTFE showed no obvious changes, like pitting or swelling, but its surface variability and the lack of distinguishing features at high magnification make it difficult to tell if the surface has changed. Our study, although preliminary, suggests that the surface structure of all these casing materials is not changed when exposed to high concentrations of organics in aqueous solution. In this respect PVC, Teflon, SS304 and SS316 were found to be suitable materials for monitoring even high concentrations of aqueous organics. Clearly exposure to pure organic solvents is another issue.

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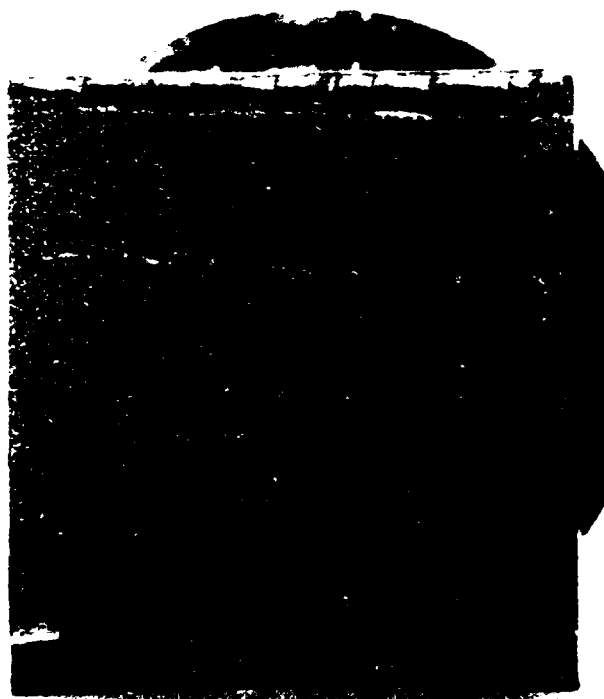
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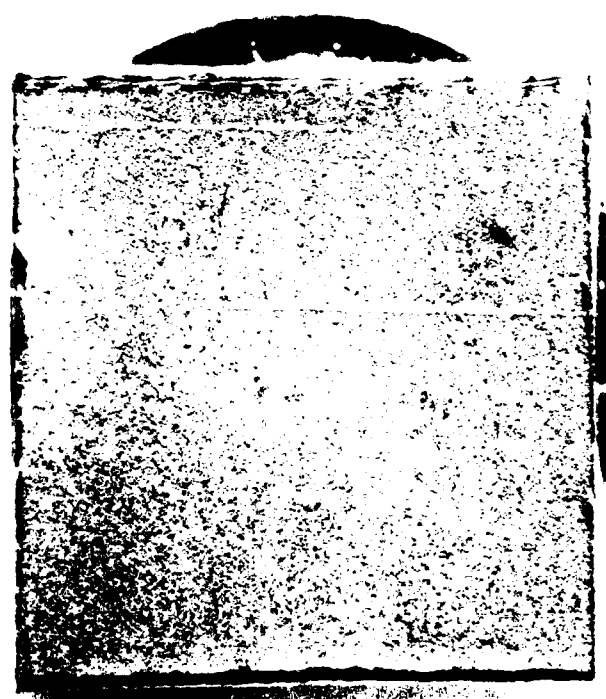
a. Teflon.



b. PVC.



c. SS316.

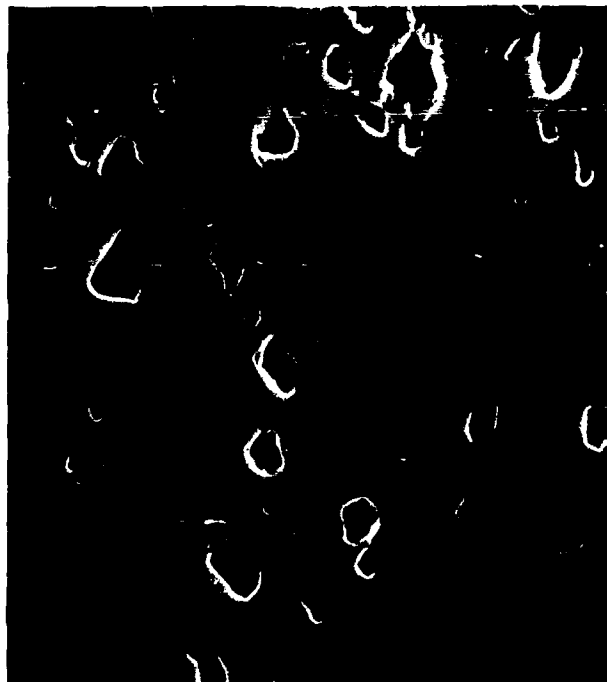


d. SS304.

Figure 1. Low magnification photographs of the four casing surfaces (8 \times).



Figure 2. SEM micrograph of untreated PVC (2000x).

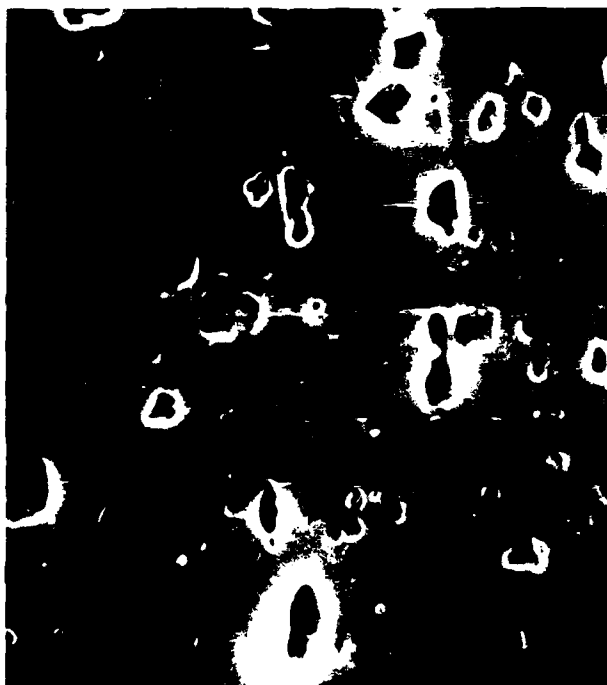


a. Soaked for 1 week.

Figure 3. Micrographs of PVC soaked in the test solution (2000x).



b. Soaked for 1 month.

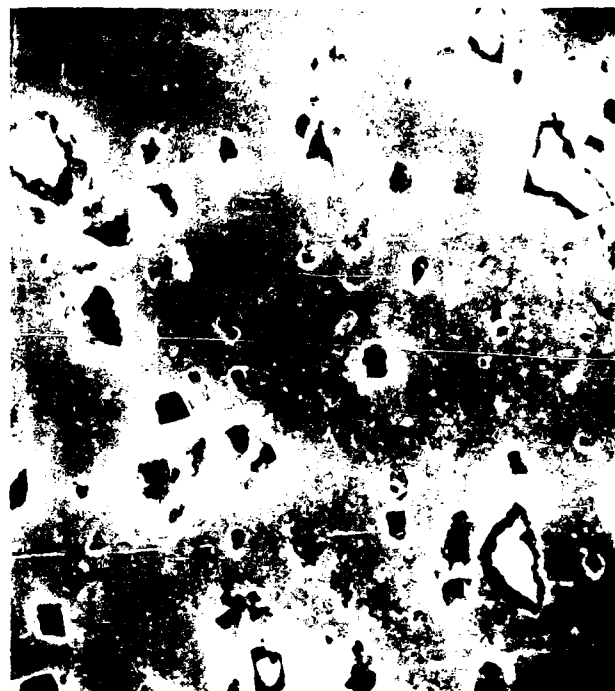


c. Soaked for 6 months.

Figure 3 (cont'd). Micrographs of PVC soaked in the test solution (2000x).



a. Soaked for 1 week.



b. Soaked for 1 month.

Figure 4. Micrographs of PVC soaked in well water (2000 \times).



c. Soaked for 6 months.

Figure 4 (cont'd). Micrographs of PVC soaked in well water (2000 \times).



Figure 5. Micrograph of untreated PTFE (200 \times).



a. Soaked for 1 week.



b. Soaked for 1 month.



c. Soaked for 6 months.

Figure 6. Micrographs of PTFE soaked in the test solution (200 \times).



a. Soaked for 1 week.



b. Soaked for 1 month.



c. Soaked for 6 months.

Figure 7. Micrographs of PTFE soaked in well water (200 \times).

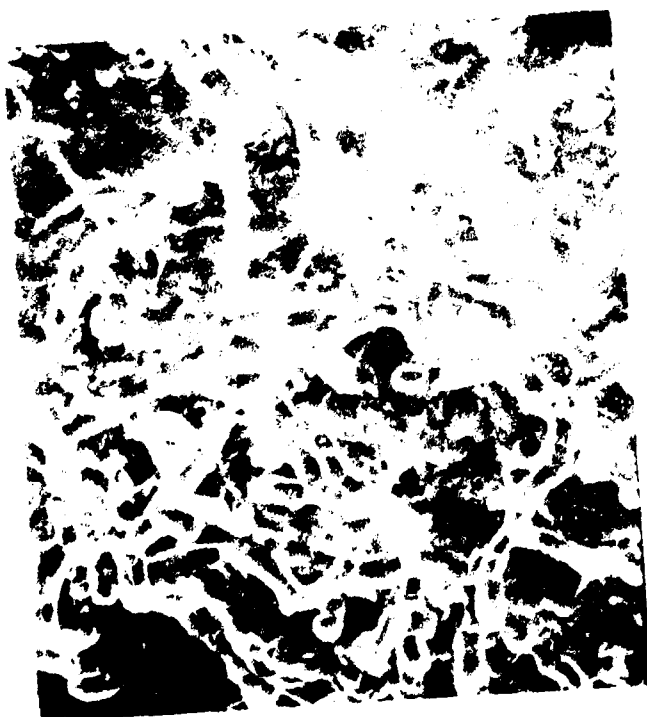


Figure 8. Micrograph of untreated SS316 (200 \times).



a. Soaked for 1 week.

Figure 9. Micrographs of SS316 soaked in the test solution (200 \times).

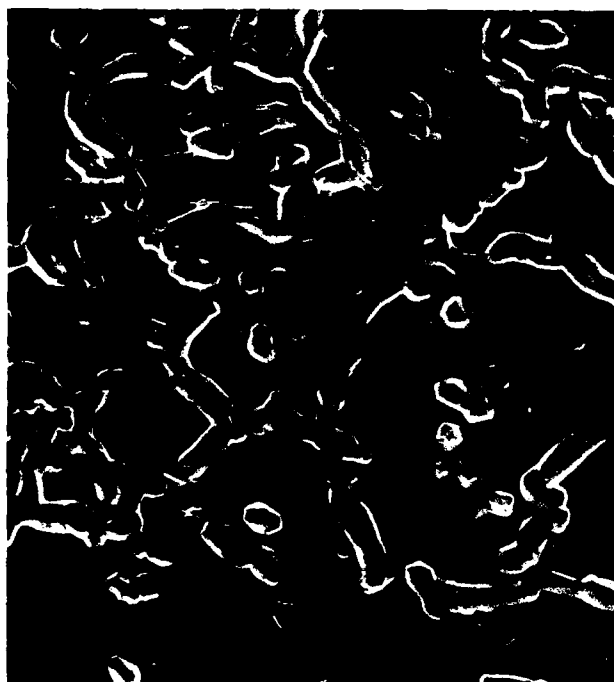


b. Soaked for 1 month.



c. Soaked for 6 months.

Figure 9 (cont'd). Micrographs of SS316 soaked in the test solution (200 \times).

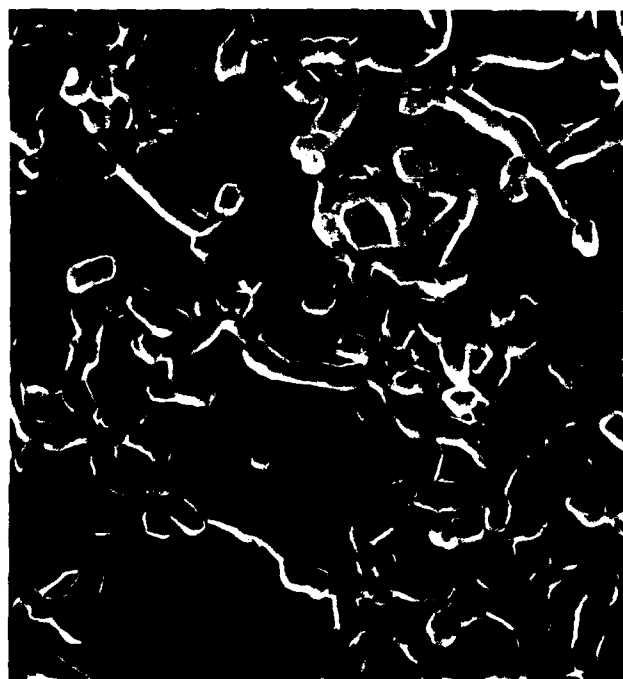


a. Soaked for 1 week.



b. Soaked for 1 month.

Figure 10. Micrographs of SS316 soaked in well water (200x).



c. Soaked for 6 months.

Figure 10 (cont'd). Micrographs of SS316 soaked in well water (200x).

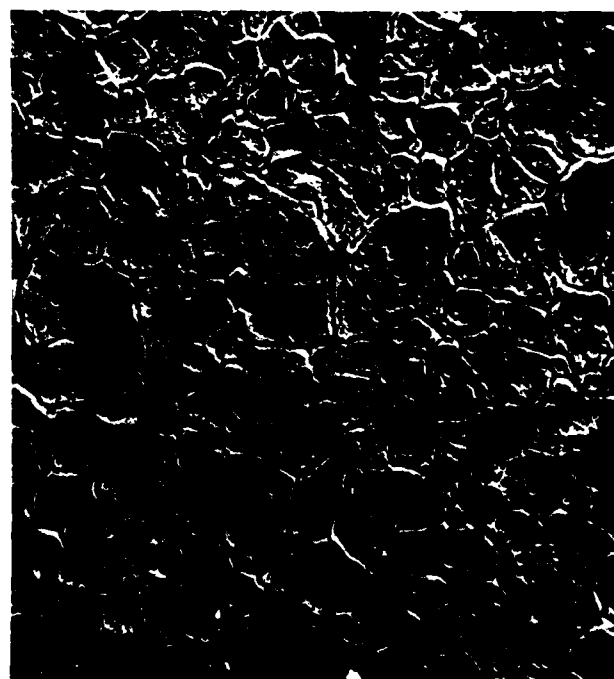
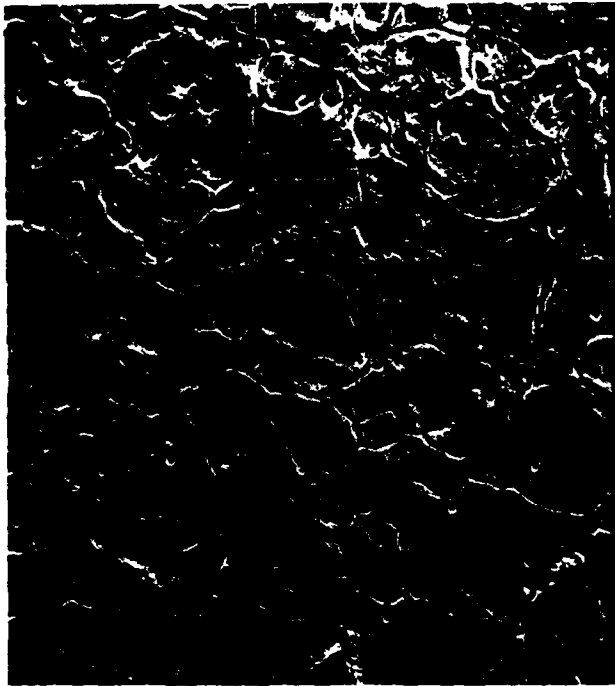
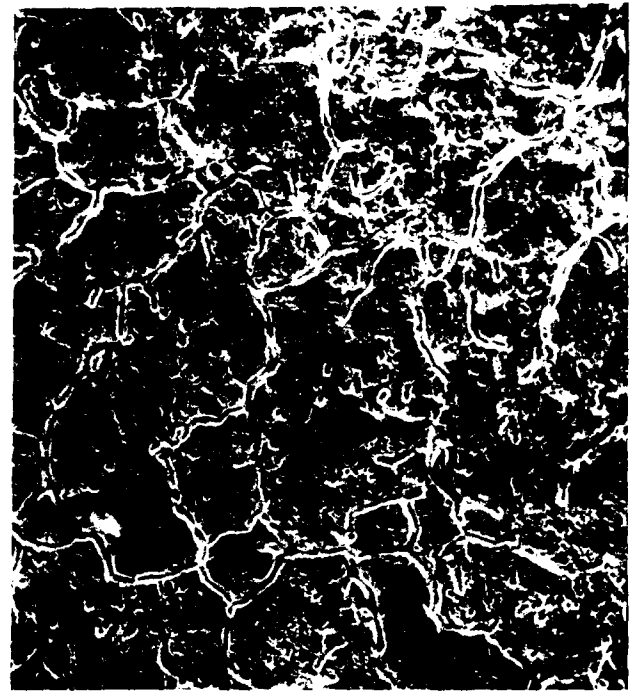


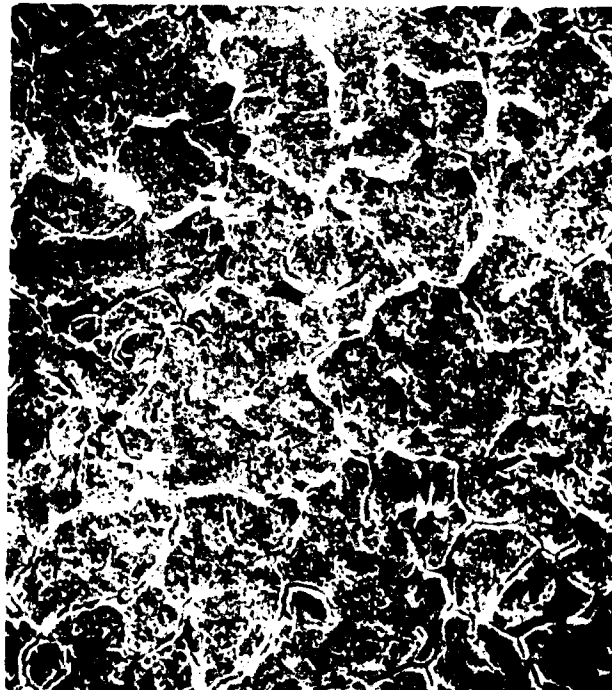
Figure 11. Micrograph of untreated SS304 (200x).



a. Soaked for 1 week.



b. Soaked for 1 month.

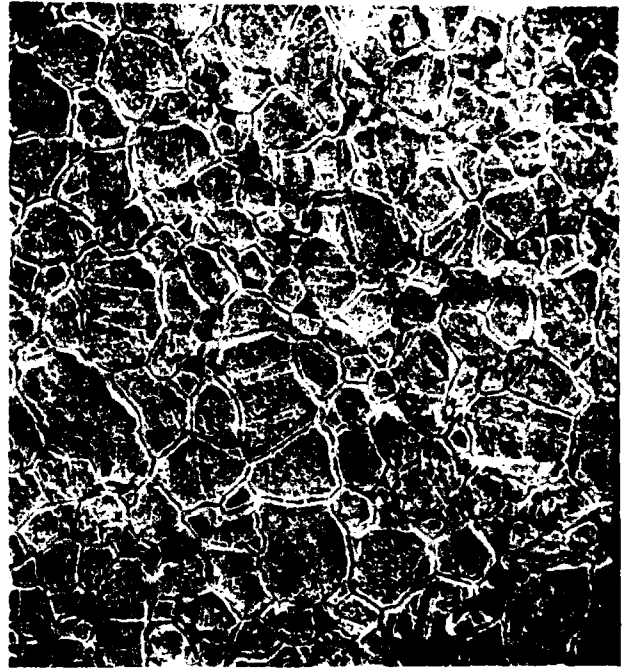


c. Soaked for 6 months.

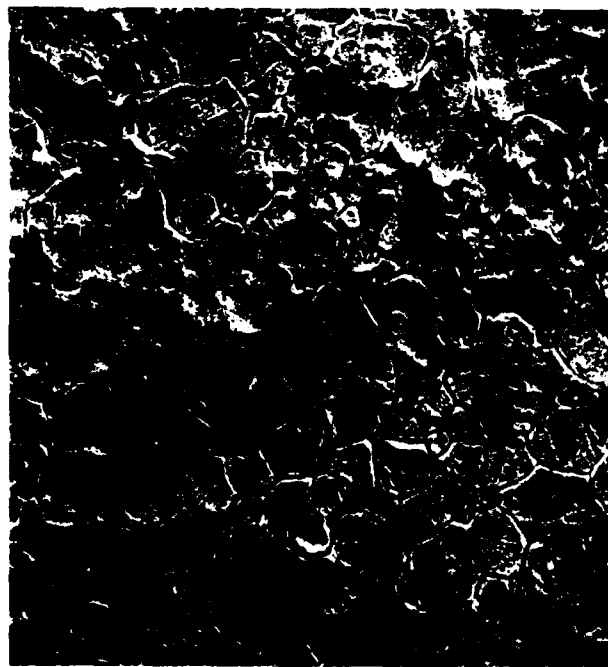
Figure 12. Micrographs of SS304 soaked in the test solution (200 \times).



a. Soaked for 1 week.

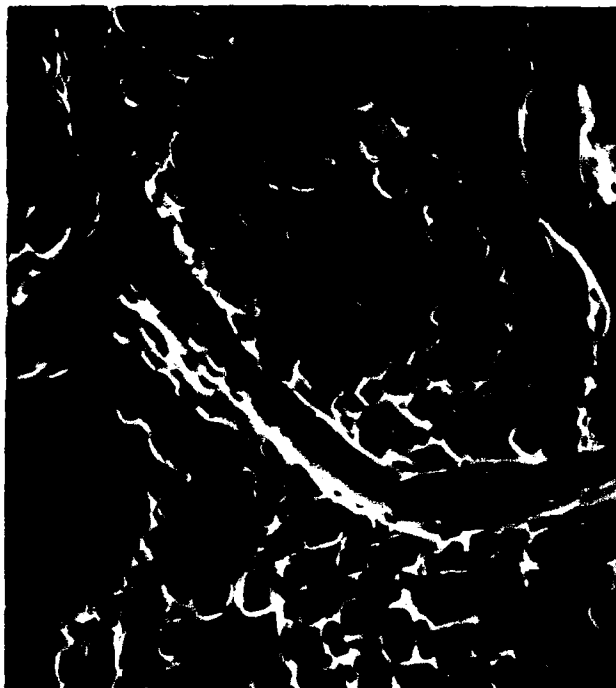


b. Soaked for 1 month.



c. Soaked for 6 months.

Figure 13. Micrographs of SS304 soaked in well water (200 \times).



a. Untreated SS304.



b. Same sample after being sealed in the test solution for 6 months.

Figure 14. Micrographs of SS304 (2000 \times)

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